

The determination by gas chromatography with atomic emission detection of total sulfur in fuels used as forensic evidence

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Abstract

In Japan, taxed diesel fuel from non-taxed fuel oil-A is illegally produced by removing coumarin, which is added as a non-taxed marker. The coumarin is removed using concentrated sulfuric acid and this produces a high viscosity and hazardous material, called “sulfuric acid pitch”, as a by-product. This compound has a detrimental effect on the environment and is hazardous to humans. The actions have been associated with organized crime with the illegally gained taxes becoming financial bases. To discriminate legal and diesel oil from illegal product, the peak area ratio R_{SC} , the ratio of total sulfur to carbon ($>C_{14}$), was used. R_{SC} is calculated by the total areas of sulfur and carbon ($>C_{14}$) from the gas chromatogram obtained by gas chromatography-atomic emission detection (GC-AED). Sulfur in legal diesel fuels is strictly regulated by a maximum limit, which was 50 ppm (and is now 10 ppm), but in the preparation of illegal diesel oil, in which coumarin is eliminated, sulfur cannot be removed. Therefore, the R_{SC} of fuel oil-A and illegal fuel oil is over 15, whereas those for legal fuel oil and diesel fuel are under 2.0. Furthermore, these ratios do not change in weathering experiments. GC-AED was applied to an actual arson case and was found to be effective for the determination of total sulfur in trace amounts of accelerants detected in fire debris at the arson scene, and hence was effective for the characterization of the ignitable liquids used.

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1. Introduction

Diesel fuel used as automobile fuel is subject to a local tax called light-oil delivery tax at the time of delivery to the purchaser. Any person who purchases diesel fuel is required to pay the tax through the contracted sellers or wholesalers from whom he/she made the purchase. The price of diesel fuel sold at gas stations includes this tax. Some businesses or users who are presumed to be associated with organized gangs (e.g. Yakuza) attempt to avoid paying the tax by mixing non-taxable kerosene or fuel oil-A with diesel fuel, or by using fuel oil-A as an alternative to diesel fuel.

In order to maintain an orderly distribution of diesel fuel in Japan through the prevention of tax evasion, coumarin has been

added for more than a decade as a marker to related oil products (i.e. to kerosene and fuel oil-A). The coumarin should be detected under the determination protocol prescribed by the Committee for the Standardization of Light-Oil Marker Analysis [1,2]. However, because this became public knowledge, tax evasion techniques have been growing more sophisticated, and include the removal of coumarin from fuel oil-A before it is sold as diesel fuel, making the discrimination of manipulated illegal fuel from legal diesel fuel difficult. The removal methods use a large amount of concentrated sulfuric acid and are therefore highly toxic and dirty.

Furthermore, through the coumarin-eliminating process, a by-product called sulfuric acid pitch, which is a highly toxic and dangerous industrial waste with high viscosity, and hydrogen sulfide are produced. These materials have caused serious environmental problems. To counter these forensic and environmental crimes, another method of discriminating illegal and legal fuels is required. The deposited “sulfuric acid pitch” container in country area and high viscosity black “sulfuric acid pitch” are shown in Fig. 1.

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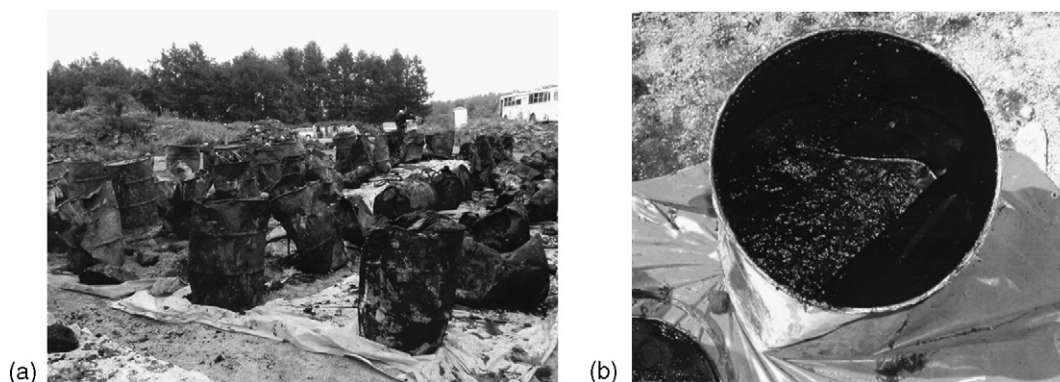


Fig. 1. Deposited “sulfuric acid pitch” container in country area: (a) high viscosity black “sulfuric acid pitch” inside the container, container was melted by sulfuric acid and (b) inside the container, high velocity black solution is “sulfuric pitch” which produces seriously dangerous H_2S .

The Japanese Industrial Standards regulate the sulfur content in diesel fuel to be less than 1/100 of the level allowed for fuel oil-A. It seems that the coumarin eliminating method cannot remove organic sulfur compounds. Therefore, the measurement of total sulfur content in the fuels may provide a means to discriminate illegal fuel produced by the removing of coumarin from fuel oil-A. The total sulfur in petroleum products is usually measured by energy dispersive fluorescent X-ray analysis or acid–base titration of sulfuric acid extracted from sulfur oxides generated from a sample burnt in a combustion tube and absorbed in hydrogen peroxide solution [3]. Both these methods require complex procedures and a large quantity of the sample.

Alternatively, gas chromatography coupled with an atomic emission detector (GC-AED) can detect certain characteristic elements contained in chemical compounds with a high degree of sensitivity and selectivity, making it possible to quantify the elements and estimate elementary composition ratios in chemical compounds. GC-AED is used in many fields because it does not require samples in large quantities [4–12]. In this report, the GC-AED method was applied to measure total sulfur contents to discriminate between legal diesel fuel and illegal fuel.

2. Experimental

2.1. Chemicals and fuel samples

Guaranteed reagents manufactured by Wako Pure Chemical Industries Co. Ltd. (Osaka, Japan) were used unaltered for all reagents. The diesel fuel samples were purchased from local gas stations: eight products from eight companies, purchased in April 2001; two products from two companies, purchased in September 2003 and 2006; and fuel oil-A from a petroleum manufacturer, purchased in July 2001 together with a product data sheet. As an illegal fuel, 10 mL of fuel oil-A was passed through a solid-phase extraction cartridge (Sep-Pak silica cartridge; Nihon Waters Co. Ltd., Tokyo, Japan), and approximately 8.5 mL of transparent yellow fuel oil was obtained.

The history of these fuels is summarized in Table 1.

In the GC-AED analysis of fuels, sulfur containing 1-benzothiophene (Wako Pure Chemical Industries Co. Ltd., Osaka, Japan) was added as an external standard for a quantitative analysis of sulfur content.

2.2. Measurement of fluorescence

Coumarin should be added to fuel oil-A as the marking material to discriminate the fuel from taxed diesel oil. Therefore, as a first step, the

coumarin-derived fluorescent spectra of fuels were measured according to the standard method [1] to determine the fuels as legal or illegal diesel fuels.

2.3. Gas chromatography-atomic emission detection (GC-AED)

The carbon, hydrogen, and sulfur contents of the diesel fuel, fuel oil-A, and illegal fuel sample were measured with gas chromatograph–atomic emission detection apparatus (Type G2350A; Agilent Technologies, Inc., CA, USA). The GC conditions are described below. A Hewlett-Packard HP-1 capillary column (25 m length; 0.32 mm inner diameter; 0.17 μm membrane thickness) was used for component separation.

The initial oven temperature was programmed at 40 $^{\circ}\text{C}$, and raised from the initial temperature to 300 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C}/\text{min}$ and then held at the final temperature for 2 min. The injection port temperature was 250 $^{\circ}\text{C}$ and helium was used as the carrier gas with a constant flow of 2 mL/min. The detection wavelength for each element was selected as 486 nm for hydrogen, 496 and 179 nm for carbon, and 181 nm for sulfur. The samples were injected in amounts of 0.1 μL using a micro-syringe. The experimental analysis was repeated three times and these quantitative values were used for calculations of carbon sulfur ratios and relative standard deviations. In the case of the identification of an accelerant in fire debris (case 2 below), a solid-phase microextractor (SPME, Supelco Co. Ltd., Bellefonte, PA, USA) was used. The fiber part of the SPME was coated with a 100- μm thick polydimethylsiloxane (PDMS). The extraction protocol was according to the manual of the solid-phase microextractor (SPME) provided by its manufacturer. The plastic bags containing fire debris were pierced with SPME fiber part and SPME fiber part was placed in direct contact with the fire debris retrieved from an arson scene for 1 min to extract accelerants and adjusted in the injection port for 2 min. The extracted compounds were introduced to GC-AED. For cases 1 and 3 outlined

Table 1
History of the sample fuels

No.	Sample	Year	Month	Manufacture
1	Diesel fuel A	2001	April	Company A
2	Diesel fuel B	2001	April	Company B
3	Diesel fuel C	2001	April	Company C
4	Diesel fuel D	2001	April	Company D
5	Diesel fuel E	2001	April	Company E
6	Diesel fuel F	2001	April	Company F
7	Diesel fuel G	2001	April	Company G
8	Diesel fuel H	2001	April	Company H
9	Diesel fuel B		Weathered 0 h	Company B
10	Diesel fuel B		Weathered 3 h	Company B
11	Diesel fuel B		Weathered 6 h	Company B
12	Diesel fuel I	2003	September	Company A
13	Diesel fuel J	2006	September	Company B
14	Fuel oil-A	2001	July	Company B
15	Illegal fuel (prepared)			

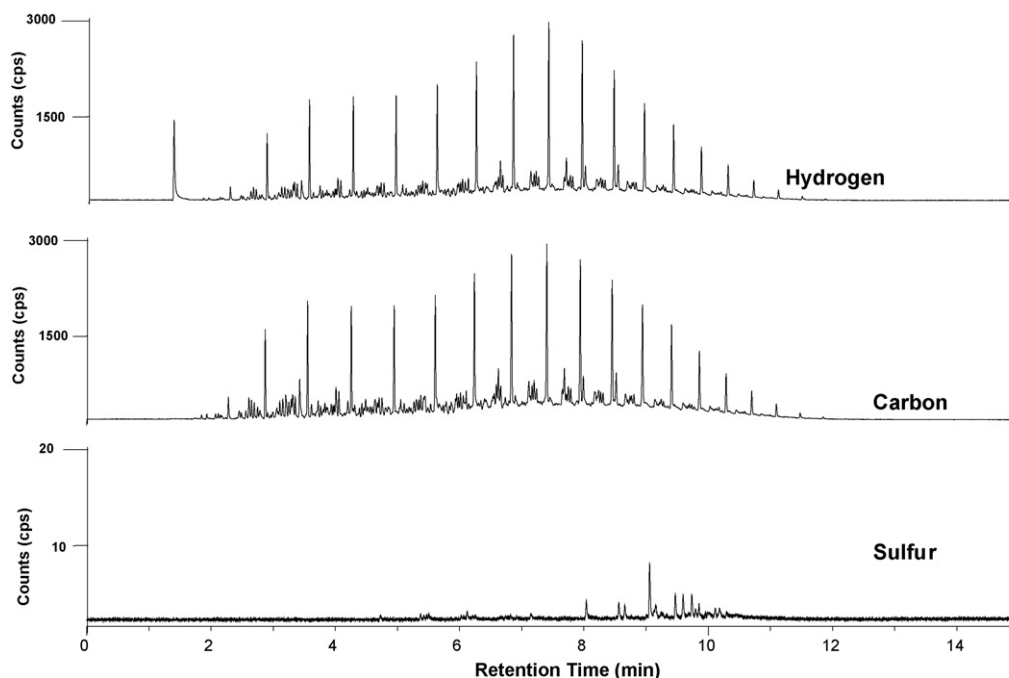


Fig. 2. Hydrogen-, carbon-, and sulfur-specific chromatograms of diesel fuel (April 2001, Company A) by GC-AED.

below, samples of an illegal fuel liquid and illegal fuel waste were injected with a micro-syringe using the same method as for the authentic samples outlined above. The external reference material, 1-benzothiophene, was liquified by heating to approximately 35 °C, and 0.02 μ L was injected.

3. Results and discussion

3.1. Measurement of fluorescence

The diesel and illegal fuel samples did not show fluorescence by the coumarin-fluorescence method. This result indicated that the diesel and illegal fuels could not be discriminated by the present recommended method [1].

Therefore, attention turned to sulfur contents for the discrimination of the fuels. The total sulfur content in each fuel is regulated in law. The total sulfur content of legal fuels was under 50 ppm (now 10 ppm), but illegal fuel produced from coumarin-removed fuel oil-A was considered to contain much higher amounts of total organic sulfur.

3.2. Gas chromatography-atomic emission detection (GC-AED)

For the qualitative and quantitative analysis of total organic sulfur contained in illegal fuel, GC-AED was applied. The

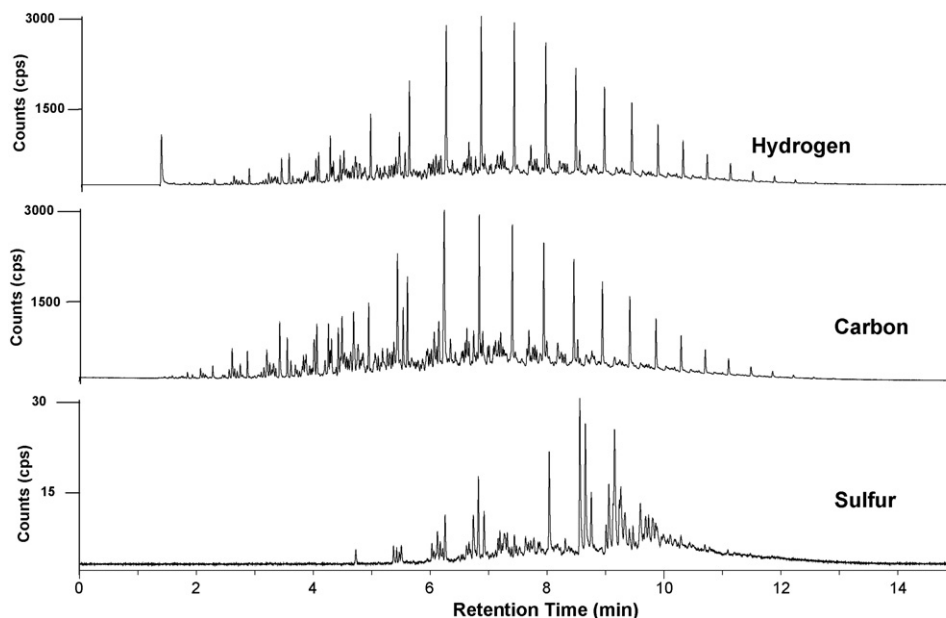


Fig. 3. Hydrogen-, carbon-, and sulfur-specific chromatograms of fuel oil-A by GC-AED.

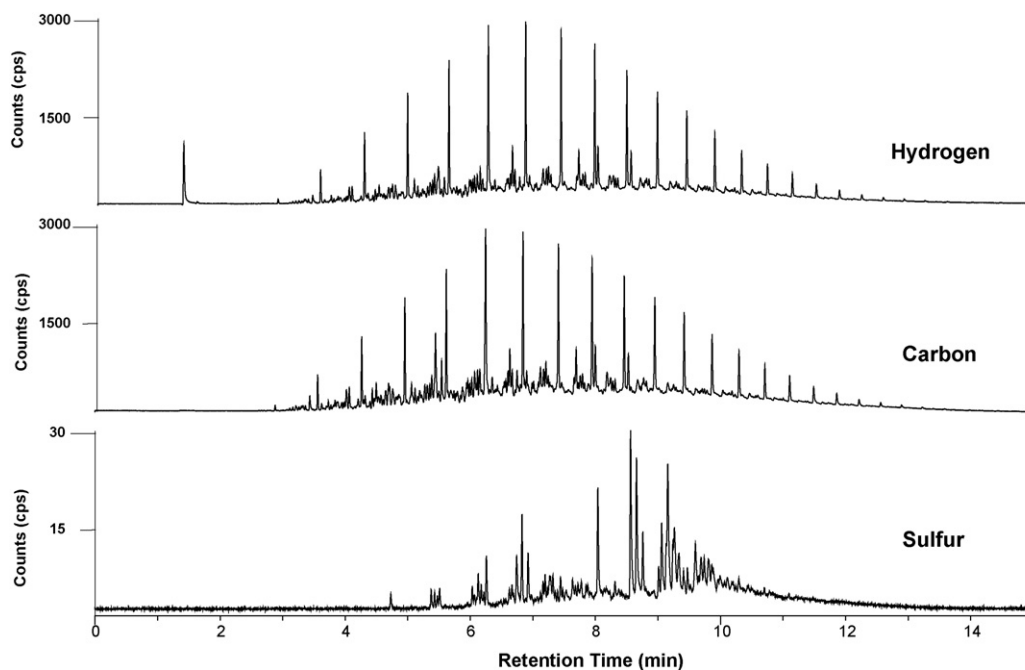


Fig. 4. Hydrogen-, carbon-, and sulfur-specific chromatograms of prepared illegal fuel by GC-AED.

chromatograms of diesel fuel (product of Company A; purchased in 2001), fuel oil-A, and illegal fuel are shown in Figs. 2–4. In the comparison of these chromatograms, that of fuel oil-A was similar to that of illegal fuel (Figs. 3 and 4). This result suggests that the simple process to remove coumarin did not cause any significant loss of carbon, hydrogen or sulfur compounds in fuel oil-A. At the same time, this result also suggests that the sulfuric acid method eliminated only coumarin, not other compounds.

The quantitative analysis of sulfur was performed using the amounts of elements detected during the measurement of the external standard, 1-benzothiophene, which was conducted

under the same conditions. The sulfur contents were calculated to be about 0.04 wt.% in diesel fuel and about 0.70 wt.% in both fuel oil-A and illegal fuel, underscoring the differences in sulfur content between the diesel fuel and fuel oil-A samples.

The sulfur content described on the product data sheet supplied by the oil company for the fuel oil-A was similar to the values measured by GC-AED. This result indicates that the sulfur content measurement in fuels by GC-AED is a suitable and satisfactory method for the discrimination of fuels, and is an alternative when the standardized sulfur determination method [3] has difficulty due to an insufficient sample quantity.

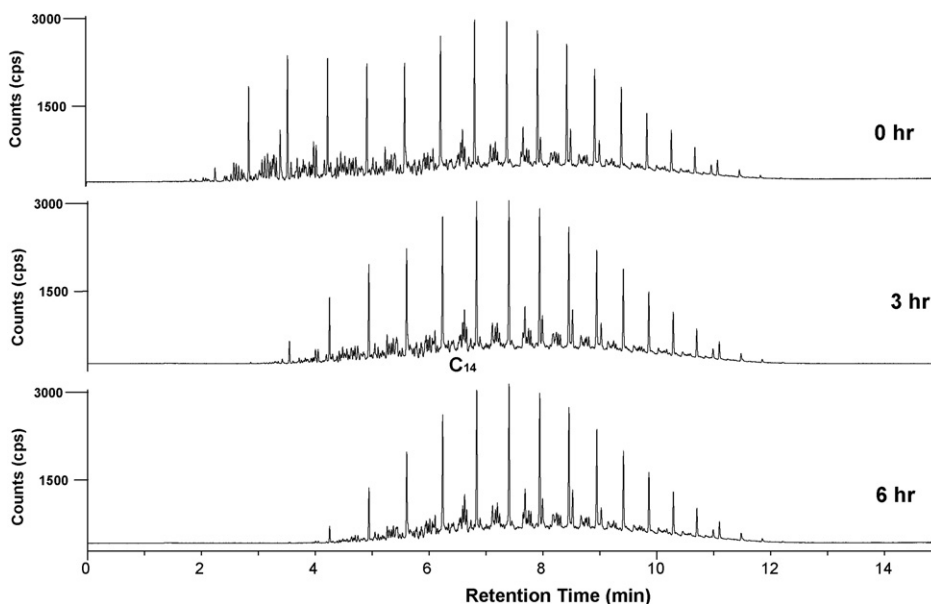


Fig. 5. Carbon-specific chromatograms of weathered diesel fuel (April 2001, Company B) by GC-AED.

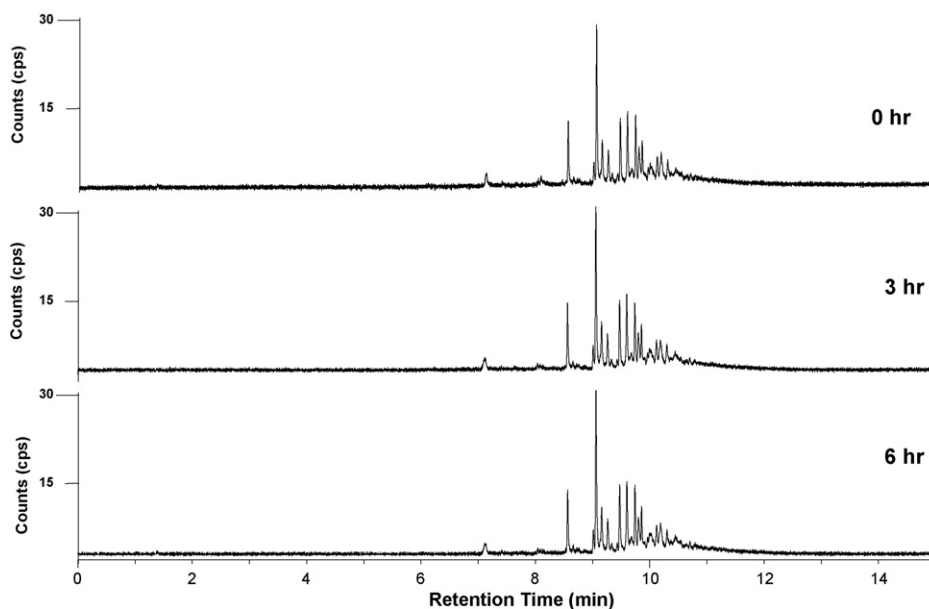


Fig. 6. Sulfur-specific chromatograms of weathered diesel fuel (April 2001, Company B) by GC-AED.

3.3. GC-AED of weathered diesel fuel and index values for discrimination

Fuel samples obtained from arson cases, submitted for examination to the Forensic Science Laboratory, are often available only as trace amounts remaining in burnt debris retrieved from fire scenes having been extinguished by water. Most have their distillation characteristics altered by partial vaporization due to the heat of the fire. Therefore, it was considered that the quantitative value of sulfur contents in such samples are far different from the content in the original fuel.

Accordingly, 5 mL of diesel fuel samples (product of Company B; purchased in April 2001) were placed in an open beaker and left to vaporize in ambient conditions on a hotplate with a temperature set at 60 °C, and measurements made at 0, 3 and 6 h. The carbon-specific chromatograms (Fig. 5) show that the vaporization process altered the distillation characteristics in the form of a significant loss of components with a boiling point lower than that of tetradecane (C₁₄).

The sulfur-specific chromatograms measured by GC-AED with the same GC column, temperature program and sampling time, did not show any significant change for either the chromatographic pattern or total sulfur content in the diesel fuel (Fig. 6).

Furthermore, in the arson case, the accelerant remaining in the fire debris was considered to be exposed to a higher temperature and the character of the accelerant may have changed. Therefore, the diesel fuel was set on the hot plate at 150 °C for 6 h. A significant difference was not observed for the sulfur-specific chromatogram for the 150 °C experiment. Therefore, the ratio of the peak areas for carbon (over C₁₄) and sulfur, after 6 min, is considered to discriminate between diesel and illegal fuels.

3.4. Calculation of R_{SC} (sulfur to carbon ratio) values

The carbon and sulfur peaks observed after 6 min were used to calculate the ratio in accordance with the following equation:

$$R_{SC} = \frac{\text{Area } S}{\text{Area } C} \times 100$$

Area *S* is the total peak area for sulfur compounds after 6 min retention time and Area *C* is the total peak area for carbon compounds after 6-min retention time. For an examination of reproducibility, GC-AED of each sample and a calculation of R_{SC} was repeated three times and a relative standard deviation (R.S.D.) was calculated. A significant difference was not observed for chromatograms of the same sample, and the R.S.D. was satisfactorily low.

Table 2
Index values of R_{SC}

No.	Sample	$R_{SC} \pm \text{S.D.}$	R.S.D.
1	Diesel fuel A	0.8 ± 0.1	12.5
2	Diesel fuel B	1.2 ± 0.1	8.3
3	Diesel fuel C	0.9 ± 0.1	11.1
4	Diesel fuel D	1.0 ± 0.1	10.0
5	Diesel fuel E	0.8 ± 0.2	25.0
6	Diesel fuel F	0.9 ± 0.1	11.1
7	Diesel fuel G	0.8 ± 0.1	12.5
8	Diesel fuel H	1.0 ± 0.1	10.0
9	Diesel fuel B	1.2 ± 0.1	8.3
10	Diesel fuel B	1.2 ± 0.1	8.3
11	Diesel fuel B	1.2 ± 0.2	16.7
12	Diesel fuel I	— ^a	— ^a
13	Diesel fuel J	— ^a	— ^a
14	Fuel oil-A	15.1 ± 0.2	1.3
15	Illegal fuel (prepared)	15.1 ± 0.2	1.3

R_{SC} and its R.S.D. could not be calculated.

^a Almost sulfur peaks were under S/N = 3.

Table 2 shows the R_{SC} and R.S.D. values calculated on the basis of GC-AED measurements of the samples of diesel fuels from individual companies, weathered diesel fuel, fuel oil-A, and illegal fuel.

The detection limit of sulfur in the calculation of R_{SC} was over 10 ppm for total sulfur content, and the signal-to-noise ratio for the limit of peak recognition in the calculation of R_{SC} was 3 ($S/N = 3$). However, using the external standard, the detection limit of 1-benzothiophene, by GC-AED (sulfur), was 10 ng of the absolute injected amounts ($S/N = 3$).

The R_{SC} values of the diesel fuel samples purchased in 2001 were about 1, which is notably different from the value for fuel

oil-A. As with the previously calculated proportions of sulfur content in the diesel fuel and fuel oil-A, samples were similar to their respective R_{SC} values. R_{SC} could be an indicator that reflects the total sulfur in fuel samples. The Japanese Industrial Standards have stipulated since 1997 that the sulfur content in diesel fuel must be less than 0.05%. With the stipulated sulfur contents in fuel oil-A (No. 1 or 2) 10 or 40 times that for diesel fuel, the R_{SC} value for fuel oil-A was estimated to be 10 or higher. In addition, the 2005 revision of the standards lowered the maximum allowable sulfur content in diesel fuel to less than 0.005. Because the R_{SC} values of the two diesel fuel products purchased in September 2003 were about 0.05, indicating that

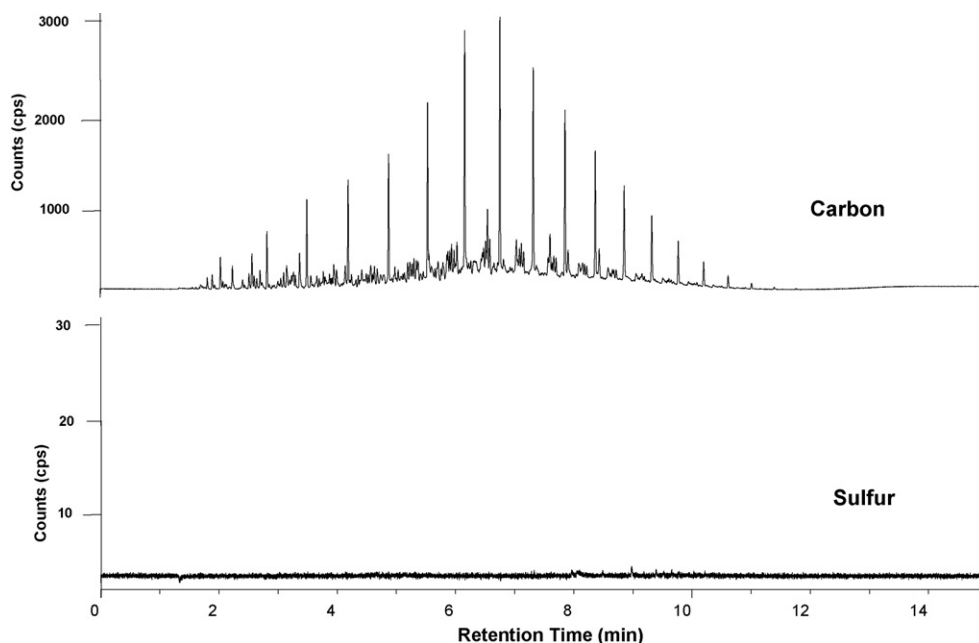


Fig. 7. Carbon- and sulfur-specific chromatograms of diesel fuel (September 2003, Company B) by GC-AED.

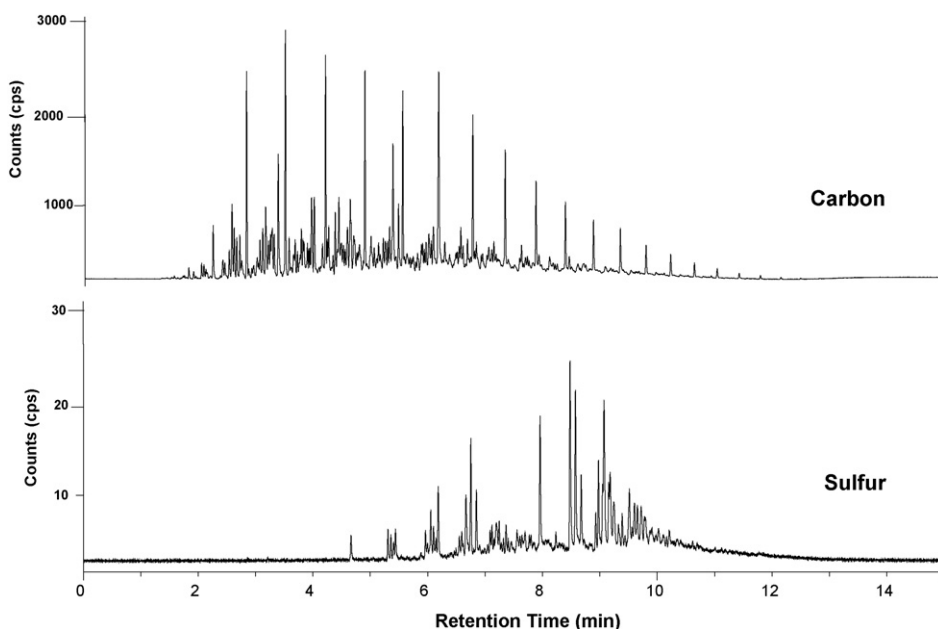


Fig. 8. Carbon- and sulfur-specific chromatograms of an oil sample (case 1) by GC-AED.

diesel fuel in distribution in September 2003 was already in compliance with the requirements of the new standard, the discrimination from fuel oil-A was likely to be more discernible. Fig. 7 shows the carbon- and sulfur-specific chromatograms of the diesel fuel samples purchased in September 2003.

The R_{SC} values of the weathered diesel fuel and the original diesel fuel were similar, as were the R_{SC} values of the illegal fuel and fuel oil-A samples. The fact that the weathered diesel fuel showed an R_{SC} value similar to that of the original fuel, even after the alteration of the distillation characteristics through vaporization, indicates that the R_{SC} index may also be

useful for the identification of accelerants detected in fire debris at an arson scene.

4. Application to actual cases

4.1. Case of local tax law violation (case 1)

This case from 2005 related to the production of illegal fuel by removing coumarin from a mixture of kerosene and fuel oil-A (both fluids are tax free) and de-coloring the product for sale as diesel fuel (taxed). Fig. 8 shows the carbon- and sulfur-specific chromatograms obtained

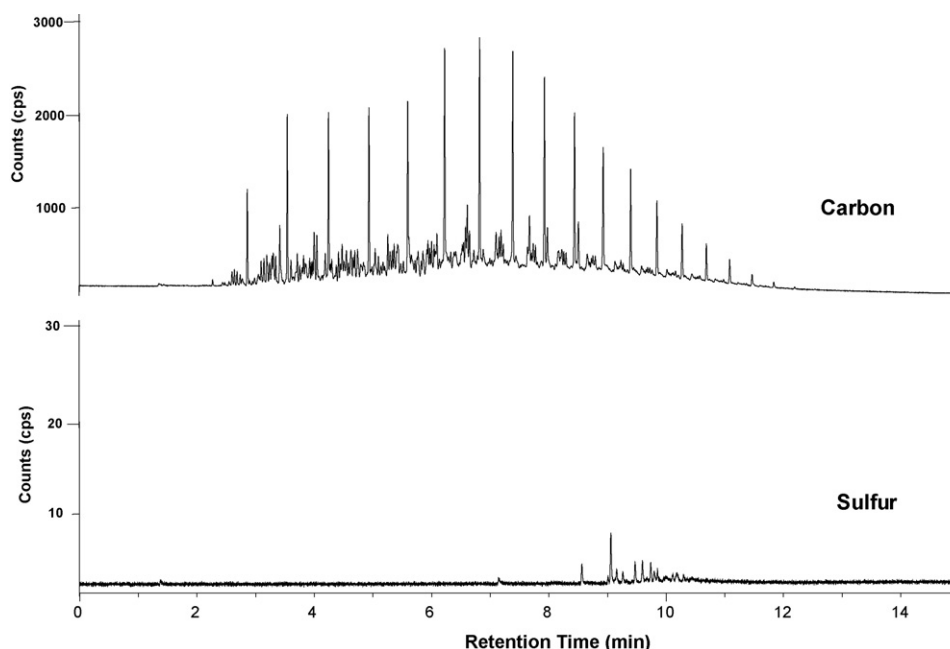


Fig. 9. Carbon- and sulfur-specific chromatograms of accelerant extracted from fire debris (case 2) by GC-AED.

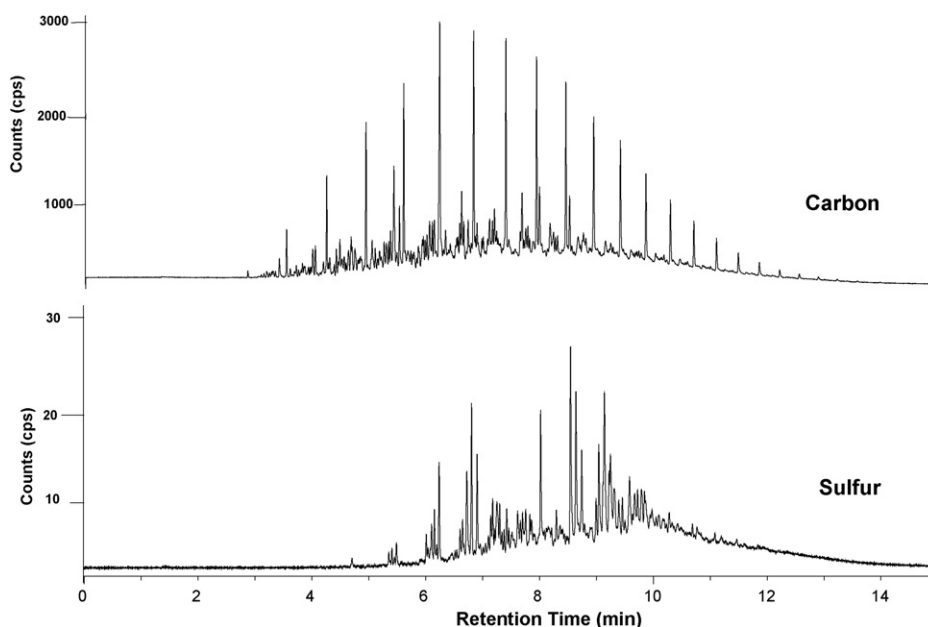


Fig. 10. Carbon- and sulfur-specific chromatograms of an oil sample (case 3) by GC-AED.

from the illegal fuel. The R_{SC} value of 12.3 was notably different from that of diesel fuel.

4.2. Case of arson in an occupied building (case 2)

This case related to arson committed by the accused who allegedly doused the employee dormitory belonging to his financially strapped company with diesel fuel and set it on fire in 2001. Fig. 9 shows the carbon- and sulfur-specific chromatograms obtained from the accelerant extracted from fire debris retrieved from the scene. A solid-phase micro-extraction method was used in which the extraction fiber of the solid-phase microextractor was placed in direct contact with the debris. The R_{SC} value of 0.9 was the same as the value for diesel fuel, which supported the statement made by the suspect under interrogation.

4.3. Case of illegal waste disposal (case 3)

This 2001 case related to the dumping in a river of a black liquid resembling waste oil. Fig. 10 shows the carbon- and sulfur-specific chromatograms obtained from the black liquid retrieved from the river. The R_{SC} value was as high as 16.6 and fluorescence spectrometry also revealed coumarin-derived fluorescence, confirming the liquid to be fuel oil-A.

5. Conclusion

The sulfur contents of fuel samples were measured by GC-AED to examine the possible application of sulfur contents to the discrimination of coumarin-removed illegal fuel from diesel fuel, which was difficult using coumarin-derived fluorescence. Though gas chromatography–inductively coupled plasma mass spectrometry (GC–ICP–MS) is a highly sensitive and accurate analytical method that measures and compares the intensity ratios of stable isotopes, it cannot be applied to measurements in the elemental analysis of sulfur using m/z 32 because of the interference of oxygen. The results of GC-AED indicated that discrimination of legal and illegal fuels was possible by measuring the sulfur contents even with only trace amounts of sample. Using the index calculated from the ratios of the carbon and sulfur contents detected in low-volatility components appearing after tetradecane, it was possible to easily discriminate

fuel types even in a fuel sample that had its distillation characteristics altered by processes such as vaporization. This method was not only effective in discrimination of accelerant types found in fire debris at an arson scene but also environmental crimes involving sulfuric acid pitch.

These results indicate that the determination of total sulfur in fuels by GC-AED is effective in the examination of forensic evidence.

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